

# Incoherent Neutron Scattering and the Dynamics of Confined Polycarbonate Films

C. L. Soles, J. F. Douglas, and W.-I. Wu

*NIST Polymers Division, Gaithersburg, Maryland 20899-8541*

R. M. Dimeo

*NIST Center for Neutron Research, Gaithersburg, Maryland 20899-8562*

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Incoherent elastic neutron scattering measurements are performed on thin (75 to 1015 Å) polycarbonate films supported on Si wafers. We find that the mean-square atomic displacement  $\langle u^2 \rangle$  is diminished by thin film confinement. For film thicknesses comparable to the unperturbed dimensions of the macromolecule, we observe two characteristic crossover temperatures in  $\langle u^2 \rangle$  as a function of temperature  $T$ , one above and the other below the bulk  $T_g$ . Furthermore, the harmonic force constant  $\kappa$ , defined by the low temperature dependence of  $\langle u^2 \rangle$  (i.e.,  $\kappa \approx k_B T / \langle u^2 \rangle$ ), increases as the film thickness decreases. These observations suggest that the atoms are more strongly localized in the thin supported films.

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A sharp rise in the scale of atomic thermal fluctuations, relative to the scale of the interatomic separation, is a general feature of the onset of fluidity in both crystalline and glassy materials. It is reasonable to expect that this ubiquitous material “softening” process is affected by thin film confinement. Changes in the softening temperature with film thickness can have particularly serious ramifications in polymer thin film applications. For example, an increased viscosity for an exceedingly thin lubrication film, such as those used in hard disk lubricants, could lead to device failure. Likewise, enhanced mobility in a thin chemically amplified photoresist film could lead to excessive photoacid diffusion and blurring of the latent lithographic image. It is then crucial to develop fundamental methods to understand finite-size effects on molecular mobility in thin polymer films.

In this Letter, we present the first incoherent elastic neutron scattering measurements to directly probe the dynamics of molecularly thin supported polymer films. The elastic scattering intensity of a harmonic solid reflects the amplitude of the thermal motions in a manner described by the Debye-Waller approximation:

$$I_{\text{inc}}(Q) \propto e^{-(1/3)Q^2\langle u^2 \rangle}, \quad (1)$$

where  $Q$  is the scattering vector and  $\langle u^2 \rangle$  is the mean-square atomic displacement. Within this framework,  $\langle u^2 \rangle$  is defined by the slope of  $\ln[I_{\text{inc}}(Q)]$  vs  $Q^2$ . While most atomic motions in soft condensed matter are characteristically nonharmonic, this approximation has proven extremely useful in synthetic [1–3] and biological macromolecules alike [4,5].

Thin polycarbonate (PC) (GE Lexan ML-4235 [6];  $M_{r,w} = 36.3$  kg/mol) films were spin cast from cyclohexanone solutions onto silicon wafers (Silicon Inc., 75 mm diam,  $N\langle 100 \rangle$ , thickness  $\approx 0.3$  mm) with freshly prepared oxide surfaces. Four sets of films with thickness values of 75, 128, 298, and 1015 Å, as determined by specular x-ray reflectivity, were studied. Approximately

13 to 15 wafers for each film thickness were broken into  $\approx (20 \times 50)$  mm<sup>2</sup> strips and placed in a cylindrical, thin-walled aluminum cell. This resulted in only 0.6 to 7.1 mg of PC in the sample cell in comparison to 52 to 58 g of Si. The cell was mounted on the high flux backscattering spectrometer (HFBS) on the NG2 beam line at the NIST Center for Neutron Research [7] and cooled to 40 K under vacuum. The spectrometer operated in the fixed window mode (stationary Doppler drive) with the elastic intensities recorded over a  $Q$  range of 0.25 to 2.0 Å<sup>-1</sup>. The sample temperature ( $T$ ) was ramped at 0.5 K/min (1014 Å films) to 0.1 K/min (75 Å films) to 525 K with the elastic intensities summed over intervals of 1 to 3 K. The HFBS energy resolution of 0.8 μeV (FWHM) implies that dynamics on a time scale of 200 MHz (approximately a nanosecond) or slower are considered static.

The neutron scattering in polymers is typically dominated by H which has a total scattering cross section approximately 20 times greater than either C or O, and nearly 40 times larger than the Si substrate. Given there is nearly 100 times more Si than PC in each sample cell, it might seem unreasonable to extract dynamical information from the polymer. However, with a neutron wavelength of 6.271 Å, the accessible  $Q$  range of the HFBS spectrometer is just below the first Bragg peak of Si ( $Q \approx 2.67$  Å<sup>-1</sup>). This ensures that the dynamics of Si are transparent to the spectrometer.

The nonlinear thermal decrease in the elastic scattering intensity in Fig. 1 demonstrates our sensitivity to polymer films as thin as 75 Å. The transmission coefficients are approximately 0.99 for all of the thin films, indicating that multiple scattering is not an issue. At each temperature, the  $\ln(I_{\text{elastic}})$  versus  $Q^2$  slope yields the mean-square displacement  $\langle u^2 \rangle$ . These linear fits are shown in Fig. 2 for the 75 Å film in the region  $Q^2 < 1.0$  Å<sup>-2</sup>. At each  $Q$ , the elastic intensities are normalized by their 40 K values, thereby setting  $\langle u^2 \rangle$  equal to 0 at 40 K. At higher  $Q$ , there is a peak, for both bulk PC and the thin films, that

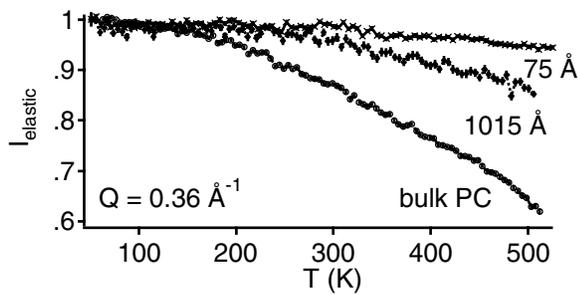


FIG. 1. The decrease in the elastic scattering intensity as a function of temperature at  $Q = 0.36 \text{ \AA}^{-1}$  for the 75 Å film, 1015 Å film, and bulk PC. The standard uncertainty from the counting statistics is less than the size of the data points.

disrupts the linear relation between  $\ln(I_{\text{elastic}})$  and  $Q^2$  (see the Fig. 2 inset for the bulk data). The peak coincides with the position of the amorphous halo for PC ( $Q^2 \approx 1.5 \text{ \AA}^{-2}$ ) leading us to believe that there is a significant amount of *coherent* scattering. Thus, we limit the fitting of our data to the low  $Q$  region ( $Q^2 < 1.0 \text{ \AA}^{-2}$ ), which effectively emphasizes the larger amplitude motions. Preliminary unpublished data indicate that these high  $Q$  features are not present in similar measurements on poly(methyl methacrylate), while similar trends are found for the dependence of  $\langle u^2 \rangle$  on film thickness.

While the  $\chi^2$  values for the linear fits are significant in Fig. 2, the average slope increases with  $T$  which leads to an increase in  $\langle u^2 \rangle$ , as seen in Fig. 3. It is evident that the relative values of  $\langle u^2 \rangle$  are *diminished* as the film thickness decreases, indicating that confinement reduces the amplitude of the atomic thermal fluctuations. This important

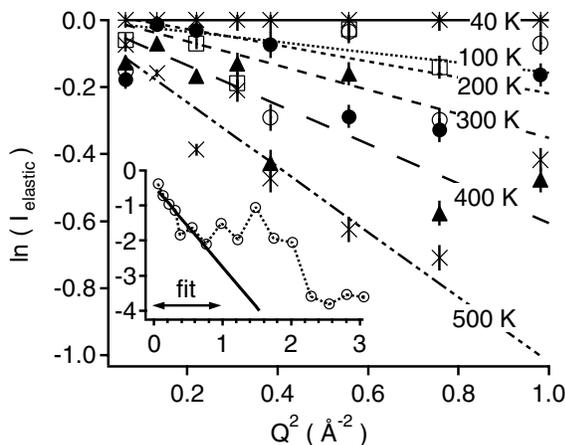


FIG. 2. The elastic intensity, normalized by its 40 K value, as a function of  $Q^2$  for the low angle detectors in the 75 Å films.  $\langle u^2 \rangle$  is proportional to the slope at each temperature. The inset reveals a maximum near  $Q^2 \approx 1.5 \text{ \AA}^{-2}$  for bulk PC. The linear fit indicates the range below this maximum used to extract  $\langle u^2 \rangle$  from the low  $Q$  data. The standard uncertainties from the counting statistics are significantly less than the point to point variations.

qualitative result is insensitive to both the details of the fits in Fig. 2 and the Debye-Waller approximation as the same conclusion can be drawn from Fig. 1; the extent of inelastic scattering is diminished with decreasing film thickness. The Debye-Waller analysis provides a framework for quantifying relative changes in  $\langle u^2 \rangle$  as a function of film thickness.

In Fig. 3 we observe a strong increase in the slope of  $\langle u^2 \rangle$  versus  $T$  in bulk PC near the calorimetric glass transition,  $T_g = 423 \text{ K}$ . This apparent softening temperature shifts to higher  $T$  as the films become increasingly thin. Breaks in  $\langle u^2 \rangle$  versus  $T$  are often observed near  $T_g$  in a wide range of glasses, as discussed in several reviews [1,2,4]. In this respect the shift of the break in  $\langle u^2 \rangle$  to higher  $T$  might be interpreted as an increase of  $T_g$  as the film becomes molecularly thin (65 Å radius of gyration). However, it is prudent to confirm this result with a technique more widely accepted as a method to measure  $T_g$  in thin polymer films.

Specular x-ray reflectivity as a function of  $T$  is commonly used to estimate the apparent  $T_g$  of thin polymer films. The Fig. 3 inset compares the thermal expansion in terms of a percent change in  $D$  normal to the surface for both a 720 Å and a 75 Å PC film on identical substrates. The break in the expansion is close to the calorimetric  $T_g$  for the thicker film but shifted to *lower*  $T$  in the thinnest film. This seems to contradict the apparent increase in  $T_g$  implied from the  $\langle u^2 \rangle$  data. However, Fig. 4 expands the vertical axis of Fig. 3 for the 75 Å film and reveals a steplike feature in  $\langle u^2 \rangle$  between 250 and 350 K. Interestingly, this steplike feature, which does not occur in films thicker than 128 Å, appears to “plateau” close to the apparently reduced  $T_g$  estimate of  $\approx 380 \text{ K}$  from x-ray reflectivity. Whether these two features are related remains to be established.

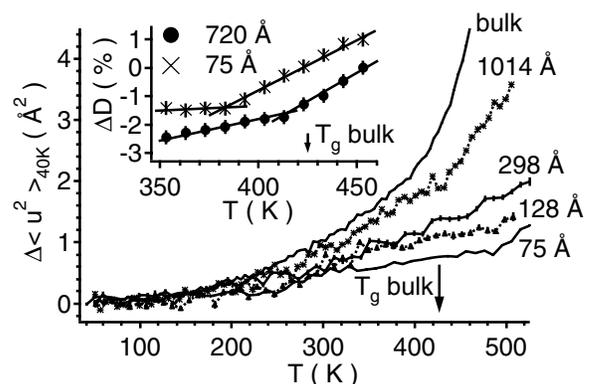


FIG. 3.  $\langle u^2 \rangle$  as a function of temperature for both bulk PC and the confined films (standard uncertainties are less than the size of the data points). There is a clear suppression of  $\langle u^2 \rangle$  with decreasing film thickness. The inset displays the corresponding thermal expansion, from x-ray reflectivity, for both a thick (720 Å) and thin (75 Å) PC film. While  $\langle u^2 \rangle$  suggests an increase of the thin film  $T_g$ , the expansion data predict a decrease.

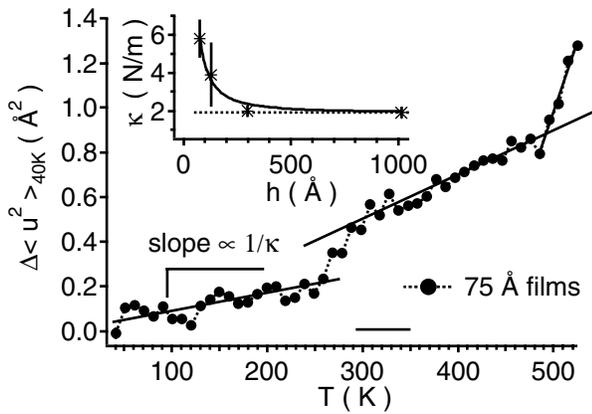


FIG. 4. The  $\langle u^2 \rangle$  data for the thinnest (75 Å) film in Fig. 3 is shown with an expanded vertical scale, revealing a steplike feature between 250 and 350 K. Below 200 K, the  $\langle u^2 \rangle$  versus  $T$  slope defines a harmonic force constant  $\kappa$ . The inset shows how  $\kappa$  stiffens with decreasing film thickness.

It is not clear how the disparate estimates of crossover temperatures in neutron and x-ray data influence the designation of the true thin film  $T_g$ . Which characteristic temperature is most appropriate to identify with  $T_g$ ? However, there is precedent for observing multiple characteristic  $T$ 's, even in bulk glass-forming liquids. Note that the high  $T$  break in the thermal dependence of  $\langle u^2 \rangle$  occurs at  $T \approx 1.2T_{g,\text{bulk}}$  for the 75 Å films. A variety of evidence [2,8,9] indicates that changes in the dynamics of supercooled liquids occur at  $T \approx 1.2T_g$ . These changes include deviations in the Stokes-Einstein and Debye-Einstein relations, a bifurcation of the  $\alpha$  and  $\beta$  relaxation processes, and the breaking of ergodicity as predicted by mode coupling theory. It seems interesting that the break in  $\langle u^2 \rangle$  for highly confined PC films also occurs near  $1.2T_{g,\text{bulk}}$ . Similarly, a sub- $T_{g,\text{bulk}}$  characteristic temperature is found by fitting viscosity or relaxation data to the Vogel-Fulcher equation (e.g.,  $\eta \approx \eta_\infty \exp[DT_0/(T - T_0)]$ ). Experimental evidence [2] and theoretical arguments by Adam and Gibbs [10] suggest that the configurational entropy stops varying well below ( $\approx 50$  K below)  $T_{g,\text{bulk}}$  near  $T_0$ . The lower temperature crossovers in both  $\langle u^2 \rangle$  and reflectivity data also occur close to a broad range of estimates ( $340 < T_0 < 375$  K) for the Vogel-Fulcher  $T_0$  for PC [11].

The ramifications of these observations need to be established by extending the measurements to a broad range of confined glasses. However, our observations raise several interesting questions. Specifically, it is not clear why the two characteristic temperatures become pronounced in the thin film geometry. The thickness dependence of these characteristic temperatures seems to indicate that confinement broadens the glass transition over a wider temperature range. Similar reports of a broadened glass transition have recently appeared in the polymer thin film literature [12].

In Figs. 3 and 4, the  $\langle u^2 \rangle$  versus  $T$  curves deviate from linearity beyond 200 K, thereby invalidating the harmonic approximation implicit in the Debye-Waller analysis. In

this anharmonic regime, the values of  $\langle u^2 \rangle$  are qualitative at best. However, between 50 and 200 K it is safe to assume that the atoms are confined to local minima in the potential energy landscape and it is reasonable to model their motions in these wells by a three-dimensional harmonic oscillator. This results in a linear increase of  $\langle u^2 \rangle$  with  $T$  (i.e.,  $\kappa \approx k_B T / \langle u^2 \rangle$ ), with  $\kappa$  defining a vibrational force constant. We find  $\kappa = 1.9 \pm 0.3$  N/m,  $2.0 \pm 0.3$  N/m,  $3.9 \pm 1.7$  N/m, and  $5.8 \pm 1.0$  N/m in the 1015, 298, 128, and 75 Å films, respectively, shown graphically in the Fig. 4 inset. The thickest films are consistent with bulk PC,  $\kappa = 1.9 \pm 0.1$  N/m, while the analogous value for pure Si is  $\kappa = 78.5$  N/m [13]. The PC  $\kappa$ 's appear reasonable given that the coefficient of thermal expansion in Si is typically 1 to 2 orders of magnitude less than most polymers; differences in the thermal expansion coefficients should track differences in elastic constants. The bulk PC force constant is also consistent with analogous measurements on proteins below 200 K [5]. Qualitatively, the increase in  $\kappa$  in the thin films suggests that the atoms are trapped in deeper potential energy minima in comparison with the bulk, or more strongly caged by their environment. This intuitive picture is sometimes used to describe a decrease in the fluid fragility in glass-forming liquids [2,4,9]. A decrease in the fluid fragility with confinement has also been suggested in other recent investigations [14,15].

In the presence of strongly anharmonic motions (i.e., above 200 K), we have discussed how the values of  $\langle u^2 \rangle$  are approximations at best. Frick and Fetters [16] demonstrate that nonvibrational motions, such as methyl group rotations, can dominate the Debye-Waller analysis in the low  $Q$  region analyzed here. In principle, details of the molecular motions can be extracted from the full inelastic neutron scattering spectra, as eloquently shown for bulk PC [17]. Unfortunately, the limited scattering signal from the thin PC films precludes a similar analysis here; the inelastic scattering intensity is several orders of magnitude weaker than the elastic. To obtain better insight into the meaning of  $\langle u^2 \rangle$  in this anharmonic regime, it is instructive to examine a more generalized (and thus complicated) representation [18]:

$$\langle u^2 \rangle = \frac{3\hbar}{2M} \int_0^{\omega_m} \frac{1}{\omega} \coth\left(\frac{\hbar\omega}{2k_B T}\right) g(\omega) d\omega, \quad (2)$$

where  $\omega$  is the frequency and  $g(\omega)$  is the density of states. In the high  $T$  limit, the quantity inside the integral is proportional to  $g(\omega)/\omega^2$ , indicating that low frequency motions significantly dominate  $\langle u^2 \rangle$ . This is analogous to x-ray crystallography where it is well known that the long range acoustic modes, not the high frequency optic modes, dominate the Debye-Waller factor. In short, the increase in  $\langle u^2 \rangle$  above 200 K is dominated by the lowest frequency motions that are still within the energy resolution of the HFBS spectrometer (faster than 200 MHz).

By their nature, low frequency, long range motions are collective across several atoms or particles. If the

mean-square displacement is dominated by the low frequency modes, the diminution of  $\langle u^2 \rangle$  with confinement primarily reflects a suppression of these collective motions. Suppressed collectivity was observed in molecular dynamics simulations on confined supercooled soft-sphere liquids [15]. Furthermore, Zorn *et al.* [19] confirm that confinement primarily affects the low frequency motions with inelastic neutron scattering experiments on salol in controlled pore glasses. The notion of decreased collectivity in molecular motion is consistent with the low  $T$  observation that the particles in the thin films are strongly trapped in deep potential energy minima. Roughly speaking, the atoms become strongly “caged” by their environment in thin films. It is more difficult for the motion of one of these strongly caged particles in the thin films to be influenced in a cooperative manner by one of its neighbors.

In closing, we note that our results are qualitatively consistent with surface forces apparatus measurements [20] on liquid films (polymer and small molecule fluids) which show a dramatic increase in viscosity  $\eta$  when the thickness falls below  $\approx 10$  molecular diameters. Furthermore, Buchenau and Zorn [21] note an exponential dependence of  $\eta$  on  $1/\langle u^2 \rangle$  liquid and glassy Se, which points to an increase in stiffness for our thinnest PC films. Similarly, increased elastic moduli [22,23] have been observed in liquid films which is an expected consequence of the increase in the harmonic force constants deep in the glassy regime. In total, these observations provide indirect evidence of stronger caging of the atoms in thin polymer films. We also emphasize that our disparate estimates of the crossover temperatures suggest that confinement effects on the glass transition in thin polymer films should be interpreted cautiously.

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